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13. ABSTRACT (Maximum 200 words) Ion transport is critical to improving the performance of conjugated polymer actuators, particularly their strain and speed. We present a novel device that allows us to measure ion transport directly and independently from electron transport in PPy films. The device geometry makes the path for ions much longer than that for electrons, ensuring that ion transport is the rate-limiting step. In addition, ion transport is visualized directly through the change in color of the film (electrochromism) as the electrochemical reaction proceeds, allowing us to precisely and quantitatively track the ion velocity. For high applied voltages, a phase front between oxidized and reduced states is observed to travel into the film, the speed of which is proportional to the applied voltage, which conclusively demonstrates that migration is the key driving force. The phase front broadens with time, which we hypothesize to be due to diffusion. At lower applied voltages, there is no phase front, showing that diffusion is the rate-limiting process. A first-cut model that contains diffusion and drift terms is postulated, and the simulation results are compared with the experimental data. This simple model predicts the intensity profiles strikingly well.			
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Enclosure 1

Final Progress Report

1 Foreword

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4 Statement of the Problem Studied

Conjugated polymers are used in actuators, displays, and batteries. In these applications, the polymer is electrochemically switched between oxidized and reduced states, and charge transport is required for this reaction. A satisfactory model that can predict the charge transport process is not yet available: research is needed to develop the constitutive equations that govern the polymer's behavior. With such an understanding of the ion transport process, it should be possible to design improved devices. In particular, an experimental method to visualize and

quantify ion transport independently from electron transport would aid model development. In this report, we present 1. a novel device configuration that allows such studies, 2. initial experimental results from using these devices, 3. a first-cut model to predict the ion transport, and 4. a comparison of experimental and modeling results.

5 Summary of the Most Important Results

5.1 Experimental design

We introduce a novel experiment that allows ion transport parallel to the surface of a conjugated polymer film to be visualized and characterized, independently of the electronic current, during electrochemical reduction and oxidation (redox). A cross-section of our experimental configuration is illustrated in Figure 2. The design has a sandwich structure with an electrode at the bottom, a conjugated polymer film in the center, and a transparent ion barrier film on the top. During redox, ions can only enter the film from sides. The conjugated polymer film will be reduced from the edges to the center. Color changes of the film corresponding to different oxidation levels will be seen through the transparent ion barrier.

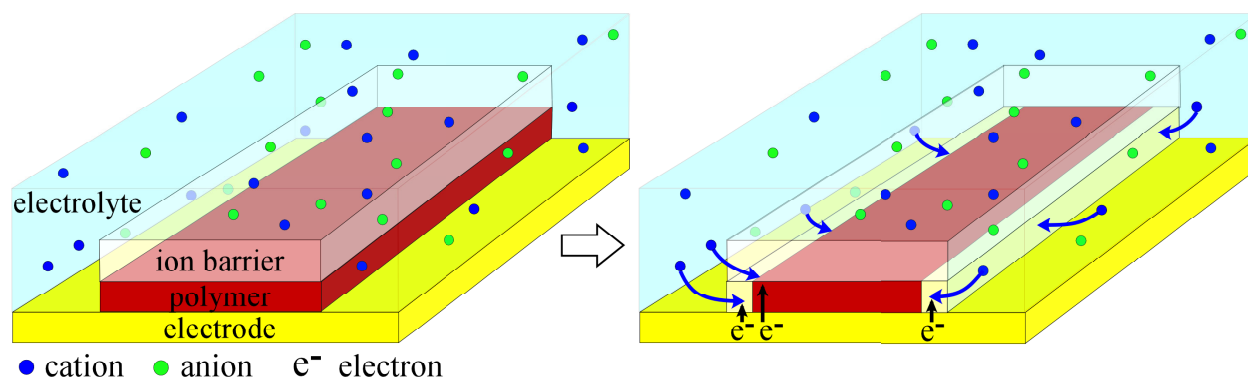


Figure 1. An experimental configuration that makes ion transport the rate-limiting step during switching of the conjugated polymer (vertical dimensions exaggerated). A thin stripe of the electrochromic material is in contact with an electrode on its bottom side, and its top side is covered by an ion-blocking layer. During electrochemical reduction (left to right), cations are transported into the film, but they can only enter from the edges. Electrons therefore have a short path, ions a long one. The polymer cannot significantly change its oxidation level until charge compensating cations arrive. The change in oxidation level results in a color change.

5.2 Experimental results

We focused initially on the reduction reaction. The potential was set to 0 V (vs. Ag/AgCl), placing the polymer in the fully oxidized state. After that, different negative potentials, varying from -0.7 to -7 V, were applied to the film to reduce it. The material system we used was polypyrrole doped with dodecylbenzenesulfonate, PPy(DBS). This is a cation-transporting material since DBS is immobile in the polymer. Overhead images of a sample reduced at -0.7 V and -1.5 V are shown in Figure 2.

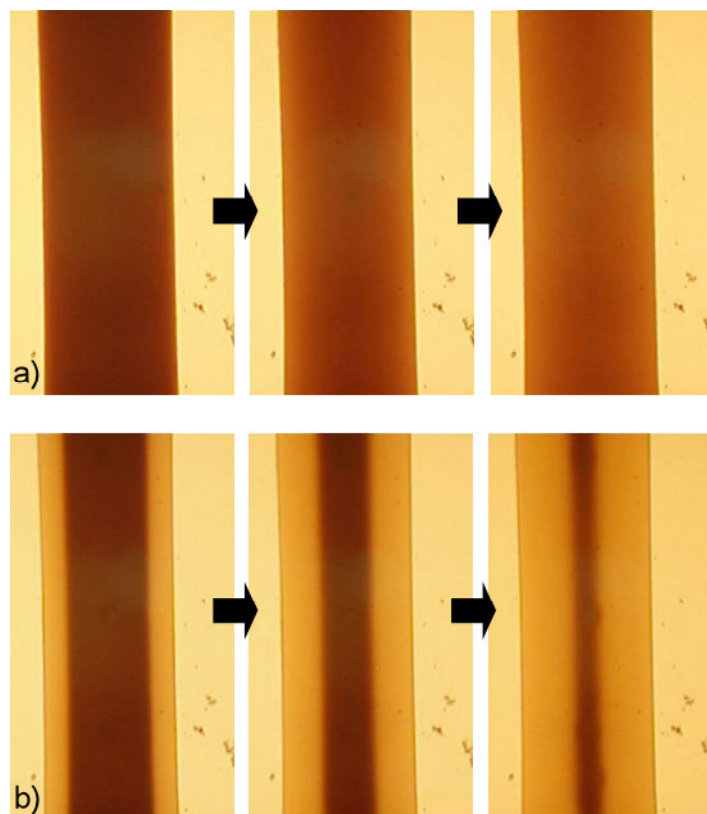


Figure 2. a) Overhead snapshots of a sample reduced at -0.7 V. Pictures were taken at 10, 20, and 30 seconds (from left to right). The color of the film gradually lightened. b) Overhead snapshots of a sample reduced at -1.5 V. Pictures were taken at 1, 2, and 3 seconds. A sharp boundary formed between the oxidized material (red) and the reduced material (transparent).

For films reduced at potentials more negative than -0.8 V, a clear boundary was formed and propagated to the center. We tracked the propagation of the boundary and obtained the velocities of this boundary at different reduction potentials, as shown in Figure 3. The velocity had a linear relationship with the applied potential between -0.8 V and -1.6 V. This result clearly told us that the potential, or electrical field, plays a very important role. (The movement of charge under an electrical field is known as *drift* or *migration*.)

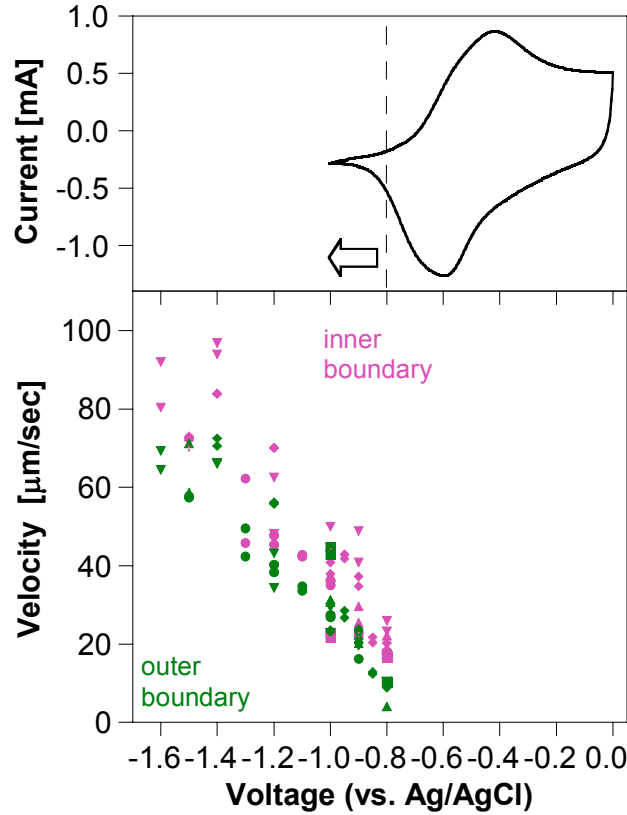


Figure 3. The cyclic voltammogram of an uncovered PPy(DBS) film shows, approximately, the applied potentials relative to the redox peaks. During reduction between -0.8 to -1.6 V vs. Ag/AgCl, the velocity of the phase boundaries vs. applied voltage was linear, showing that migration dominates the charge transport. Different symbol shapes correspond to different samples, repeated symbols indicate duplicate runs on the same sample. Above -0.8 V, no phase boundaries were observed, and below -1.6 V, the velocity saturated at ~ 70 $\mu\text{m/sec}$.

5.3 Modeling

A first-cut model that includes both diffusion and drift is presented below. The first equation gives the change in concentration of the ions:

$$1. \quad \frac{\partial C_i}{\partial t} = -\nabla \cdot \vec{J}_i = -\nabla \cdot (-D_i \nabla C_i - z_i \mu_i C_i \nabla \phi),$$

where t is time, J_i is the flux of species i (mol/sec- cm^2), C_i is the concentration (mol/ cm^3), D_i is the diffusion coefficient (cm^2/sec), z_i is the charge number, μ_i is the mobility ($\text{cm}^2/\text{V-sec}$), and ϕ is the electrical potential. Maxwell's equations give the potential in terms of the net charge density:

$$2. \quad \epsilon_0 \nabla(\epsilon \nabla \phi) = Q = C_i - e,$$

Where ϵ_0 is the permittivity of a vacuum, ϵ is the dielectric constant of the conjugated polymer, and $Q = C_i - e$ is the net charge density. When charge neutrality does not hold ($C_i \neq e$), there is a resulting electric field in the polymer that is the driving force for ion transport. The equations were solved in FEMLAB with only a single spatial dimension.

5.4 Comparison of experimental and modeling results

The simulation results were compared with experimental color (red-channel intensity) data in Figure 4.

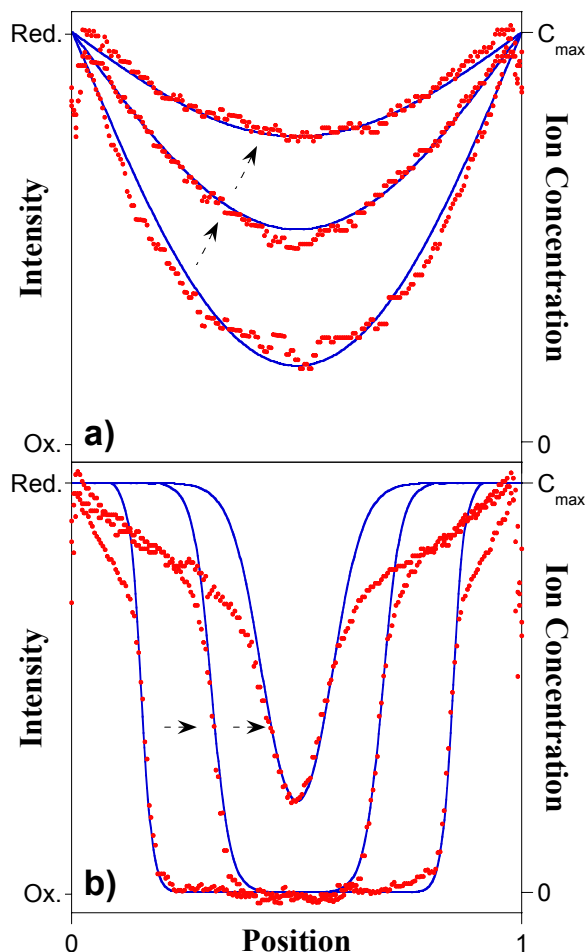


Figure 4. Experimental data (red points) vs. modeling results for ion concentration (blue line). The edges of the film are positions 0 and 1. The intensity minimum is for the fully oxidized state, and the maximum is for the fully reduced state. a) Applied potential = -0.7 V (vs. Ag/AgCl); data at 30, 60, and 90 seconds. Modeling curves are *not* equally spaced in time. b) Applied potential = -1.5 V; data at 0.6, 1.5, and 2.4 seconds (0.9 seconds apart). The modeling curves are again not equally spaced in time.

This simple simulation predicted the existence of phase fronts when drift dominates the ion current, and it did a remarkably good job of capturing the shapes of the intensity profiles for both low and high diffusion. However, it did not correctly predict the front velocities or the diffusion-like phenomenon behind the front. In future work, the model will be modified to include additional physics.

6 List of Publications and Technical Reports

6.1 Papers published in peer-reviewed journals

None

6.2 Papers published in non-peer-reviewed journals or in conference proceedings

None

6.3 Papers presented in conference meetings but not published in conference proceedings

Invited talk to be presented in March and an extended abstract to be published in the proceedings:

Xuezheng Wang, Elisabeth Smela, and Benjamin Shapiro, “Understanding Ion Transport in Conjugated Polymers”, Proceedings of SPIE Conference: Electroactive Polymer Actuators and Devices, March 14-18 2004, San Diego, CA, USA.

6.4 Manuscripts submitted but not published

Xuezheng Wang, Elisabeth Smela, and Benjamin Shapiro, “Understanding Ion Currents in Conjugated Polymers”, Advanced Materials, submitted Feb 2004.

6.5 Technical reports submitted to ARO

N/A

7 Participating Scientific Personnel

Xuezheng Wang, GRA with Elisabeth Smela

Elisabeth Smela, Assistant Professor, Mechanical Engineering, University of Maryland

Benjamin Shapiro, Assistant Professor, Aerospace Engineering, University of Maryland

8 Report of Inventions

None

9 Bibliography

N/A

10 Appendix

Manuscript submitted to Advanced Materials:

Xuezheng Wang, Elisabeth Smela, and Benjamin Shapiro, “Understanding Ion Currents in Conjugated Polymers”, Advanced Materials, submitted in Feb 2004.